On the Post-Curing Thermal Treatment of Silicone Rubbers: A Study on Electrical Performance

O. Vryonis1\*, T. Andritsch1, A.S. Vaughan1, P. Morshuis2, A. Claverie3

1Tony Davies High Voltage Laboratory, School of Electronics and Computer Science, Faculty of Engineering and Physical Sciences, University of Southampton, SO17 1BJ, Southampton, UK

2Solid Dielectric Solutions, Leiden, the Netherlands

3Single Buoy Moorings Inc., Marly, Switzerland

\*Correspondence to: O. Vryonis (Email: [O.Vryonis@soton.ac.uk](mailto:O.Vryonis@soton.ac.uk))

# ABSTRACT

Silicone rubbers, particularly poly(dimethylsiloxane) (PDMS), are popular across various industrial applications, however notable issues arise from volatile cyclic siloxanes and their tendency to compromise their performance. This study investigates the electrical performance (DC conductivity, dielectric spectroscopy, DC breakdown) of two commercial PDMS products, before and after a post-curing treatment (200◦C, 4h). The tested materials, named PDMS A (RTV) and PDMS B (LSR), are chosen as they display distinct characteristics: they differ in terms of outgassing behavior and structural alterations during treatment. In particular, thermogravimetric analysis (TGA) reveal pronounced volatile removal in PDMS B, while Fourier transform infrared (FTIR) and Raman spectroscopy demonstrate pronounced structural alterations in PDMS A (crosslinking of unreacted long chains) promoted by post-curing. As expected, the electrical insulation performance is enhanced in both post-cured materials: the magnitude of this depends on the extent of two abovementioned aspects. The DC conductivity reduction follows the volatiles removal pattern (larger scale in PDMS B), while the *ε’* and *ε’’* values reduce following the structural alteration pattern (elimination of a relaxation peak in PDMS A). The DC breakdown strength enhancements are driven by structural variations rather than removal of volatiles.

# KEYWORDS

Polydimethylsiloxane, PDMS, silicone rubber, post-curing, cyclic volatiles, dielectric properties, electrical performance

# INTRODUCTION

Silicone rubbers also known as polysiloxanes or silicones are semi-inorganic elastomers typically used as outdoor high voltage (HV) insulation,1 flexible dielectric transducers,2 as well in soft devices and microfluidics,3 in the automotive and aerospace industries and various medical or domestic products.4 Polysiloxanes comprise one of the most flexible backbones known featuring the SiRR’O repeat unit in which the Si-O bond displays bond lengths of 1.64 Å compared with 1.53 Å in C-C bonds 5 and 1.43 Å in C-O bonds.6 Moreover, the Si-O-Si bond angles are about 143o and readily passing through the linear 180o state as compared to the typical 110o tetrahedron angles. These molecular characteristics bestow polysiloxanes high levels of flexibility combined with excellent electrical and thermal insulation properties, resilience to weathering and hydrophobicity, low surface free energy and high gas permeability, to name a few.4,5

Perhaps the most popular polysiloxane is poly(dimethylsiloxane) or PDMS, featuring the [-Si(CH3)2O-] backbone, with a vital role in industry and a wide array of applications.7 PDMS is a thermoset material and can be crosslinked via three different routes8,9 including (a) moisture-based condensation, (b) addition (known as hydrosilylation) and (c) radical (often, but not limited to, peroxide-initiated) reactions. Condensation-based products display slow curing times while, in certain cases, the crosslinking could even be reversed when exposed to high temperatures,10 while peroxide-based systems are considered toxic when compared with other components.11 Therefore, the addition reaction is preferable offering advantages such as thermally stable products8,12 and higher degree of control on the network topology.13 In PDMS compounds hydrosilylation involves reaction between vinyl (CH=CH2) groups often found at long chain ends and hydride (Si-H) groups found in methylhydrosiloxane-based crosslinkers, in the presence of platinum-based catalysts,14,15 as well as inhibitors to regulate the reaction time (pot life).16 Several grades of commercial PDMS systems are available in the market featuring various performance characteristics.3 Most of them are two-component products (require mixing parts A & B)10 and fall into one of the following categories: (a) room temperature and (b) high temperature vulcanising rubbers commonly known as RTV and HTV, respectively.2 As the name suggests RTVs offer the ease of curing at ambient temperatures even though the process could be accelerated at elevated temperatures. On the contrary, HTVs are cured strictly at high temperatures and are further divided in other sub-categories, such as high-consistency rubbers (HCR) and liquid silicone rubbers (LSR). As far as electrical applications are concerned, such as outdoors HV insulation17,18 and dielectric elastomer transducers,19–21 RTV and LSR products are most commonly used, with LSRs featuring higher molecular weight and therefore viscosity. HCR components are even more viscous and display high stiffness levels which might be a limiting factor for dielectric applications. 22

As mentioned above, PDMS can be utilized as a high-performance material, however this is realized only when reinforced with relatively large amounts of fillers, since it is an inherently weak elastomer.23 Even though in some cases PDMS is reinforced with “soft” fillers (immiscible liquids),24 or blended with miscible liquids,25 the vast majority of commercial products are filled with relatively high contents of “hard” fillers (nanoparticles), traditionally silica (SiO2) due to inherent compatibility26 and drastic improvement in mechanical performance.27 Such effects have been exhaustively reported in the published literature.28–30 Pendant, or even “neutral” (non-reactive) PDMS chains could also be incorporated as plasticizers.13 The complexity of PDMS compounds is exacerbated even further by the fact that commercial products are formulations intentionally kept unknown, as trade-secrets.31

A prominent issue with polysiloxanes is their synthetic process and its high yield in by-products. Typically, the first synthetic step is a nucleophilic substitution of chlorosilanes that results in low molecular weight siloxanes; those could be linear or cyclic. The second step is an equilibrium reaction, either acid- or base-catalyzed that results in high molecular weight chains.2 The disadvantage of this process is that cyclic oligomers are retained within the final product. In the case of dimethylsilicones, such as PDMS, the residual cyclic oligomers might reach up to 15% of the final product’s mass.32 Typically, this process is followed by vacuum degassing, even so most commercial products retain a certain amount of low molecular weight cyclic siloxane oligomers (often referred to as volatiles). Those moieties are named after their chemical structure, so that cyclic trimers (hexamethylcylotrisiloxane), tetramers (octamethylcyclotetrasiloxane), pentamers (decamethylcyclopentasiloxane), are referred to as D3, D4, D5, respectively, and so on, where D is the Me2SiO2/2 repeat unit, and the numeral designates the number of those.33 These residual volatiles remain mobile even within the crosslinked PDMS, and tend to gradually outgas to the compound’s surface, including device interfaces, etc. While the latter effect could be advantageous in certain cases (for instance hydrophobic recovery), in other cases it might lead to contamination and other related issues.34

The most facile method to drive volatiles out of PDMS is high temperature post-curing thermal treatment. Especially, in cases where silicones would be in contact with human skin, such as personal care products, regulatory agencies require proof of small volatile content; one of the most stringent requirements (German regulatory agency35) stipulates that a “conditioned” silicone should not release more than 0.5 wt.% of volatiles when heating at 200 ◦C for 4 h. As such, a few studies have examined the effect of equivalent post-curing treatments on PDMS. Rothka et al.36 reported on the types of moieties outgassed during post-curing, optimisation of treatment techniques as well as effect of specimen thickness, filler content, etc. Brook et al.37 further investigated factors affecting devolatilization, such as specimen thickness, surface area, contact and transpiration, while they also reported on the effect of pre- and post-treatment on the tensile performance of silicone compounds. Significantly, it was found that thermal treatment (dubbed devolatilization) of the constituents before the mixing and crosslinking stages was not particularly beneficial.37 Lothongkam et al.38 attempted ageing of silicone rubbers at 200 ◦C for up to 100h and observed that the early stages (initial 4 hours) of the process resulted in increased AC breakdown strength. Zakaria et al.39 performed pre-stretching of silicone rubbers for various timespans up to three months, revealing a gradual decline in elastic modulus attributed to outgassing of cyclic volatiles and suggesting that post-curing might be required. In another study34 they performed post-curing (at 200 ◦C) for time spans up to 4 hours and observed an increase in elastic modulus although they claimed that no further crosslinking took place during the thermal treatment; additionally, the electrical breakdown strength values were found to increase proportionally to the tensile modulus. These effects were attributed primarily to removal of cyclic volatiles: no further structural/chemical insights were given.

Even though post-curing in silicone rubbers is commonly acknowledged as beneficial, it is often overlooked with suppliers typically recommending only a *quick* curing process. Additionally, only a few studies have signified the importance of post-curing in improving PDMS performance and even fewer focus on electrical insulation properties, which as stated earlier are of significant importance on applications such as HV insulation and elastomeric transducers. This study set out to demonstrate the effect of the post-curing process mentioned above (200 ◦C, 4 hrs) on the electrical insulation performance of two commercial PDMS compounds and correlate it to chemical and/or structural alterations promoted by the treatment. The main focus is to establish associated structure/property relations, not demonstrated in the related literature yet. The PDMS products chosen for this study represent the categories of: (i) RTV (named PDMS A) and (ii) LSR (named PDMS B) which are the most widespread, as mentioned earlier, in electrical insulation applications.

# EXPERIMENTAL

## Materials & Sample Preparation

Both PDMS compounds used in this study are two-component systems, crosslink via platinum-catalyzed hydrosilylation reactions and, as mentioned above, will be referred to as PDMS A (RTV, viscosity: 3,500 cP) and PDMS B (LSR, viscosity: 550,000 cP). These two compounds are widely used in the industry and research sectors and even though it is known that there might be batch variations among silicone materials we believe that the two selected compounds are representative of the RTV and LSR categories. Both PDMS systems have been identified as components incorporating hexamethyldisilazane-treated (methylated) silica while PDMS A also incorporates some degree of vinyl-treated silica. While we would expect that the presence of the latter may cause reactions and variations on the crosslinking density, among other things, we did not investigate this possibility any further (for example solvent swelling experiments40), since the unknown exact composition of PDMS A and B would render interpretation speculative. Sample preparation involved mixing parts A and B with the use of a planetary mixer (FlackTek DAC 330-110 SE), operating at 2,000 rpm for 20 sec. Once the mixing process was complete, the homogenised mixtures were applied onto flat PTFE surfaces with an Elcometer 3580 Casting Knife Film Applicator. Acquired film thicknesses were 150 ± 5 μm. The curing process was conducted in accordance with the respective suppliers’ recommendations: 150 ◦C for PDMS A and 175 ◦C for PDMS B; both for 10 min. Regarding post-curing, it should be noted that the supplier of PDMS A does not suggest that any such treatment be performed, while the supplier of PDMS B recommend post-curing at 200 ◦C for 4 h. We treated all the prepared specimens at 200 ◦C for 4 h to meet the “conditioned” silicone requirements35 mentioned above. The term post-curing is commonly used as the rubber has already set (and is therefore in an elastomeric state) upon the curing step that comes first. Equivalent terminology is used in other thermoset materials, such as epoxy resins.41 Other terms such as: “devolatilization” have also been used37 in the literature.

## Characterization Methods

Fourier transform infrared (FTIR) spectroscopy was conducted using a Nicolet Summit X FTIR Spectrometer (Thermo Fisher Scientific), operating in attenuated total reflection (ATR) mode using an Everest ATR optical base accessory. The examined spectral region was 525 – 4000 cm-1. A total of 16 measurements were averaged, per sample, while background checks were done in advance. The obtained spectra were then standardized for comparison.

Raman spectroscopy was performed with a Renishaw RM1000 confocal microprobe system (12.5 mW, 785 nm) at a range of 100 – 3200 cm-1. Calibrations were performed in advance using a silicon wafer specimen (520 cm-1).

Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer Pyris 1 system in two different modes: (i) temperature ramp up to 900 ◦C at 10 ◦C/min in nitrogen environment and (ii) isothermal at 200oC, in air environment, for 4 h. The first mode was performed to assess the thermal decomposition profiles, while the second mode was performed to emulate the post-curing conditions and assess its effect on the volatile content.

DC conductivity tests were performed using an in-house built apparatus, comprising a Glassman series EH (20 kV) high voltage source and a Keithley 486 Picoammeter. The tests were undertaken at 20 kV/mm and each specimen was electrified for 20 min in total. The test cell comprises a measurement electrode featuring a diameter of 30 mm surrounded by guard ring (1 mm gap).

Dielectric spectroscopy was performed via two different instruments each focusing on: (i) room temperature low frequency regime and (ii) fixed frequency over a wide temperature range. For the former an Omicron SPECTANO 100 Dielectric Material Analyzer was used, operating at 200 VRMS over a frequency range of 10-4 Hz – 5 kHz. For the temperature dependent tests, a Solartron 1296 dielectric interface combined with a Schlumberger SI 1260 impedance/phase gain analyzer (VRMS = 7 V, operating at 1 Hz) and a Janis Research STVP-200-XG cryostat were used. The temperature was controlled with a Lake Shore 332 cryogenic temperature controller over a range from −180 ◦C to 200 ◦C, in steps of 10 ◦C. The tests were conducted in a helium atmosphere and the cooling fluid was liquid nitrogen. The cryostat chamber was vacuum purged and backfilled with helium gas three times prior to the measurements to ensure no moisture was trapped within.

The DC breakdown tests were conducted using an in-house built apparatus42 featuring a test cell comprising of ball-shaped electrodes, 6.3mm in diameter, vertically arranged, so that no additional pressure (for instance spring-loaded, etc.) was exerted. The PDMS samples were placed between the electrodes and then submerged into silicone oil and subjected to a 500 V/s ramp until breakdown occurred. For each sample, twenty breakdown events were recorded which were then analyzed via the Weibull probability distribution function, using OriginLab.

# RESULTS AND DISCUSSION

## Structural and chemical comparison between PDMS compounds

The structural and chemical characteristics of PDMS A and PDMS B were contrasted via FTIR and Raman spectroscopy, as well as TGA to highlight the differences between these two compounds. To avoid interference from cyclic volatile species, FTIR and Raman spectroscopy were performed only on the post-cured compounds, in this section. The results are presented below.

### Fourier transform infrared spectroscopy

Figure 1 shows a comparison between the infrared spectra of the two post-cured products. Several peaks can be observed in both systems largely overlapping and broadly resembling those found in the related literature.43–46 Nevertheless, subtle differences can be observed between the two systems with the most prominent absorption bands being: 2962 cm-1 (stretching of methyl groups); 1011 cm-1 (asymmetric deformation of Si-O-Si); 788 cm-1 (asymmetric stretching of C-Si-C) and 751 cm-1 (rocking of methyl groups); as well as the 843 cm-1 – 863 cm-1 band region (asymmetric stretching of C-Si-C and rocking of methyl groups, respectively).47 The latter has also been used as a reference band43 since it represents vibrations stemming from the polymer backbone. Here we refrained from that since the compositions and chemistry of the two PDMS systems are not known to be equivalent. From these it is apparent that PDMS A is consistently displaying stronger methyl-related bands than PDMS B, while the latter displays slightly stronger and broader Si-O-Si vibrations. Consider first the methyl concentration variations: it is reasonable to assume that the vast majority of methyl groups within a PDMS component stem from the polymer backbone; even though some of the signal is presumably pertinent to the methylated silica surfaces. Nevertheless, silica fillers should in principle be Si-O-Si rich rather than anything else. Under this assumption PDMS A displays higher concentration of polydimethyl-based backbone macromolecules than PDMS B, which we interpret as lower silica filler content. Consider now the Si-O-Si concentration variations: PDMS B displays not only stronger, but also broader (at the low frequency tail) 1011 cm-1 band than PDMS A. In general, the intensity of that band region is strongly affiliated to the chain molecular length and/or branching.48 For instance, small silicon-based molecules, such as POSS, display a single band located at about 1070 cm-1,49 while polysiloxanes with longer chains or higher degree of branching, would demonstrate overlapping and more complex Si‑O‑Si bands.48 Furthermore, as mentioned above, silica fillers are expected to be richer in Si-O-Si bands rather than bands pertinent to surface functionalities. Under this assumption PDMS B, that displays stronger and more complex Si-O-Si band than PDMS A, is more likely to be characterised by larger chain molecular weight (*Mw*), and/or higher degree of chain branching and/or higher silica filler content than PDMS A.

Another notable difference between the two tested materials is the band area at 1190 cm-1, that appears as a pronounced shoulder in PDMS B. This band is typically ascribed to symmetric stretching of methoxy groups (Si-OCH3) which are not unheard of in PDMS systems, since methoxy-containing substances, such as polymethylmethoxysiloxane (PMOS), or methoxy-functionalised PDMS can be found in commercial products.8,44,50

To sum up, the differences in FTIR spectra described above indicate that:

* PDMS A features lower silica content than PDMS B, which is rather reasonable considering the viscosities of those products.
* PDMS B is likely featuring higher: (i) *Mw* or (ii) degree of branching, or (iii) dispersion of molecular lengths than PDMS A.
* PDMS B possibly displays increased methoxy concentration, compared with PDMS A.

Another minor difference between the two tested systems is that PDMS A displays two additional weak absorption bands at 2920 cm-1 and 2850 cm-1 (see inset in Figure 1). These were found to be pertinent to the post-curing treatment and will be discussed later.



Figure 1. FTIR spectra comparison between the post-cured tested PDMS components.

### Raman spectroscopy

Figure 2 shows the Raman spectra of the two post-cured PDMS compounds. Bands characteristic of PDMS51 can be seen at: 488 cm-‑1 (Si-O-Si symmetric stretching); 687 cm-1 (Si-CH3 symmetric rocking); 708 cm-1 (Si- C symmetric stretching); 788 cm-1 (CH3 asymmetric rocking & Si-C asymmetric stretching); 860 cm-1 (CH3 symmetric rocking); 1264 cm-1 & 1412 cm-1 (CH3 symmetric & asymmetric bending, respectively) and 2907 cm-1 & 2965 cm-1 (CH3 symmetric & asymmetric stretching, respectively). The acquired Raman spectra align well with the FTIR ones shown in Figure 1 since PDMS B displays pronounced Si-O-Si -related and weaker methyl-related (either CH3, Si-CH3 or Si-C) bands compared with PDMS A. For instance, the I488/I708 intensity ratios are: 1.39 and 1.52 in PDMS A and PDMS B, respectively, while the I488/I2907 ratios are 3.62 and 5.62, respectively. To add to that, PDMS A features two Raman bands at ~616 cm-1 (strong) and ~755 cm-1 (weak) that have been associated with the Si-C bond;52,53 these bands are, respectively, weak and absent in PDMS B.



Figure 2. Raman spectra comparison between the post-cured tested PDMS components.

### Thermogravimetric analysis (thermal decomposition)

Figure 3 shows the TGA thermographs of the two tested PDMS compounds. Evidently, these materials show considerably different residues at 900 ◦C (Figure 3a), with PDMS A displaying smaller values (46%) than that of PDMS B (73%). It has been established elsewhere54 that the catalyst, that is still contained in the cured elastomers, promotes chemical reactions while the PDMS thermally decomposes, and converts it (or the associated silica filler) into silicon oxycarbide (SiOC). This then converts to silicon carbide (SiC) at even higher temperatures (> 1000 ◦C). The silica surface chemistry is also participating and promoting chemical reactions with the surrounding environment; residue content has been claimed54 to be the highest with vinyl-treated surfaces among other functionalities. Nevertheless, the abovementioned statement is contradicted here since PDMS A (incorporating some degree of vinyl-treated silica) displays smaller residue than PDMS B (filled only with hexamethyldisilazane-treated silica). We infer that, as suggested by the related literature,54 higher silica content (PDMS B in this study as seen in FTIR and Raman spectroscopy above) results in higher thermal decomposition resistance and higher char residue, which is in good agreement with the findings of the present study. Another possibility could be variations in the catalyst contents which, in the case of the compounds tested here, are unknown.

The associated derivative TGA thermographs (DTG) are depicted in Figure 3b, where notable variations are also evident. PDMS A displays a single decomposition mechanism centered at 540 ◦C, while PDMS B shows two different degradation mechanisms located at 428◦C and 700◦C, respectively. These behaviours align well with the published literature55 concerning vinyl- and methyl- terminated PDMS and associated crosslinkers. Generally, the thermal degradation of silicone rubbers has been suggested to be convoluted, featuring three or four different mechanisms that do not take place independently,46 and will not be discussed further in the present study.



Figure. 3. TGA decomposition (a) and DTG (b) thermographs of the tested PDMS components.

Other, smaller, thermal events are evident in both specimens at temperatures between 100 - 300 ◦C in Figure 3b. It can be observed that the two tested PDMS components display different characteristics in this temperature range, which might be ascribed to volatile species and the associated variations on the amount of those moieties. These will be discussed in the section below.

## Effect of post-curing

The effect of post-curing on the two tested compounds was assessed via isothermal TGA scans, FTIR and Raman spectroscopy, as well as DC conductivity, dielectric spectroscopy and DC breakdown tests. The results are presented below.

### Thermogravimetric analysis (Isothermal 200 ◦C, 4 h)

Figure 4 shows the isothermal TGA thermographs, emulating the post-curing conditions. It can be observed that these materials undergo a swift mass reduction within the initial 15 min, with the effect continuing at a slower rate until the end of the 4 h treatment. This finding is in good agreement with the published literature.36 The mass losses recorded within 15 min of the isothermal test were: ~0.7% in PDMS A and ~3% in PDMS B, while the total mass losses (after 4 h) were 1.7%, and 3.5%, respectively. It appears that the suggested curing process provided by the suppliers are not sufficient to remove enough volatiles for the resulting materials to be classified as “conditioned silicones”, as described above. Furthermore, it is evident that even though PDMS A appears to display lower thermal degradation resistance than PDMS B (see Figure 3) potentially attributed to lower silica content, it also appears to retain less cyclic volatiles within its volume. Zakaria et al.34 suggested that highly filled PDMS compounds display pronounced retention of volatiles (thus outgassing more during post-curing), which is in good agreement with the findings of the study presented here.



Figure 4. Isothermal TGA thermographs at 200 ◦C of the tested specimens.

### Fourier transform infrared spectroscopy

The effect of post-curing on the FTIR spectra of PDMS A and PDMS B can be seen in Figures 5 and 6, respectively. Considering first PDMS A: only relatively small magnitude variations are apparent upon post-curing with the most prominent one being the absence of the Si-H deformation peak (910 cm-1 region). The latter means that this product displays a population of unreacted crosslinker hydrides in its bulk, which disappear upon thermal treatment. In contrast, there is no evidence of unreacted terminal vinyl groups (-CH2=CH2) that would normally appear in the ~1600 cm-1 region.48,56 An excess of hydrides is to be expected in commercial products, which constitutes “common practice” to guarantee attachment of all the long PDMS chains13 and prevent formation of pendant network branches. The complete elimination of excess hydrides is also common (only upon post-curing here) since they react with one another via hydrolysis and condensation reactions, forming so called “highly crosslinked domains”.13 Additionally, post-cured PDMS A shows a minor decrease in the Si-O‑Si band, particularly the shoulder located at 1065 cm-1, compared with its counterpart pre-post-curing. This could possibly be associated with the removal of low *Mw* cyclic moieties. While D3 cyclics display a single Si-O-Si band around 1020-1010 cm-1, the respective band appears at higher frequencies, up to 1090-1075 cm-1, in D4 and D5 before widening and splitting in even larger cyclic siloxanes.48 The reduced absorption intensity at 1065 cm-1, is consistent with the removal of cyclic molecules possibly larger than D3 which is in good accordance with the related literature reporting on removal of, primarily, D6 – D8 during post-curing37 and D4 – D9 when exposed to corona discharges.57 The abovementioned studies deployed gas chromatography to characterise the oligomers, instead. Furthermore, post-curing in PDMS A generates two additional absorption bands located at 2920 cm-1 and 2850 cm-1 (see inset in Figure 5). To our knowledge, these bands are not characteristic to every PDMS system and are typically ascribed to asymmetric and symmetric stretching of CH2 groups.58,59 Such groups normally form during crosslinking via reaction of hydrides with vinyl groups, however that would not explain why such a feature is not observable at all in PDMS B (see below). The explanation for this could be a low temperature decomposition effect (below 400 ◦C) which is often considered negligible in PDMS, however it constitutes the very first step of thermal decomposition. The latter phenomenon entails a heavy crosslinking step especially of chains adsorbed on the silica surfaces, as well as release of small molecules such as H2 or methane.54 Since both mentioned mechanisms result in the formation of ethylene radicals (-CH2∙), it is reasonable to assume that the post-curing treatment considered here is sufficient to initiate this decomposition stage in PDMS A. This finding is in good agreement with the TGA decomposition results shown in Figure 3 and the suggestion that PDMS A displays poorer thermal decomposition resistance than PDMS B.



Figure 5. FTIR spectra of PDMS A, before and after post-curing.

The effect of post-curing on the FTIR spectra of PDMS B is shown in Figure 6. PDMS B displays similar features with PDMS A: (i) a relative decrease in absorption magnitude of the shoulder at 1065 cm-1; (ii) total elimination of the band at the 910 cm-1 region; (iii) no evidence of unreacted terminal vinyl groups (region ~1600 cm-1). Nevertheless, as shown in the inset in Figure 6, this system does not display the two absorption bands at 2920 cm-1 and 2850 cm-1, meaning that the post-curing treatment is not initiating the early-stage decomposition described above. It is confirmed that PDMS B is more thermally resistant than PDMS A for reasons discussed above.



Figure 6. FTIR spectra of PDMS B, before and after post-curing.

The results presented here are in good accordance with the isothermal TGA thermographs in Figure 4, suggesting the removal of low *Mw* cyclic volatiles, even though the variations in absorbance intensity in the 1065 cm-1 shoulder are subtle. Nevertheless, FTIR is quite insightful in revealing the: (i) existence of unreacted crosslinker hydrides, as well as (ii) early-stage thermal degradation of compounds with low thermal decomposition resistance, such as PDMS A.

### Raman spectroscopy

The effect of post-curing on the Raman spectra of PDMS A and PDMS B can be seen in Figures 7 and 8, respectively. Considering first PDMS A, the cured elastomer displays a small band at ~2152 cm-1 which is attributed to the reactive Si-H bonds;43 the post-curing treatment results in elimination of this band which aligns well with the FTIR spectra shown above. Additionally, cured PDMS A displays a weak band (see inset in Figure 7) at ~1600 cm-1; typically attributed to vinyl groups (CH=CH2),43 which also disappears after post-curing. This finding suggests that, despite the excess of crosslinker hydrides, PDMS A does not fully form its network structure with simple curing, potentially leading to some long, pendant chains (or unreacted vinyl groups on the vinylated silica surfaces) remaining in the network. Some other slight variations in bands related to methyl groups (616 cm-1, 687 cm-1, 1412 cm-1, 2907 cm-1) are also observed and could be attributed to the initiated degradation that PDMS A undergoes during post-curing, as discussed above.



Figure 7. Raman spectra of PDMS A, before and after post-curing. The spectra shown in the inset have been vertically shifted apart for ease of viewing.

The effect of post-curing on the Raman spectra of PDMS B is shown in Figure 8. The only observable variation induced by the post-curing treatment is the Si-H band at 2152 cm-1 (see inset in Figure 8), confirming that PDMS B also displays unreacted hydride groups before post-curing occurs. Here the 2152 cm-1 band, before the post-curing, is weaker than its counterpart in PDMS A, suggesting fewer unreacted hydrides. In contrast, there is no evidence of unreacted vinyl groups, or any other effect induced by the post-curing treatment in PDMS B.



Figure 8. Raman spectra of PDMS B, before and after post-curing. The spectra shown in the inset have been vertically shifted apart for ease of viewing.

The Raman spectra presented here are in good accordance with the FTIR spectra shown above, suggesting the incomplete reaction of crosslinker hydrides and, in the case of PDMS A, vinyl groups before post-curing. PDMS A is also expected to feature long pendant chains before post-curing.

### DC conductivity

Figure 9 shows the DC conductivity of the two silicone elastomers measured before and after post-curing. PDMS A (Figure 9a) displays conductivity values of ~3.3 x 10-16 S/cm and ~2.3 x 10-16 S/cm before and after the thermal treatment, respectively. In contrast PDMS B (Figure 9b) displays conductivity values of ~6.8 x 10-16 S/cm and ~7.3 x 10-17 S/cm before and after the thermal treatment, respectively. Evidently the post-curing treatment is beneficial in both cases by reducing charge transport, especially in PDMS B featuring a substantial decrease by an order of magnitude. Based on the analytical methods described above, the increased charge transport before post-curing is likely to be associated with the existence of volatile species, since the most pronounced observed variation in conductivity is displayed in the system with the largest mass loss during post-curing (PDMS B, see Figure 4). In contrast PDMS A is seemingly unaffected by the initiated degradation shown in the FTIR spectra (see Figure 5), which would be expected to increase charge transport. Additionally, the existence of unreacted hydrides (in both PDMS A and B) and terminal vinyl (in PDMS A) groups could be a contributing factor. However, it is not consistent with the observed behaviour - if that was the case, PDMS A would be featuring more dramatic changes due to the existing long pendant chains and the incomplete crosslinked network.

Overall, a comparison between conductivity values obtained by the two post-cured and therefore volatile-free systems reveals rather low charge transport values in PDMS B, compared with PDMS A. This might be attributed to the higher silica content in PDMS B, (as shown in FTIR and Raman results) and aligns well with our previous study highlighting decreasing DC electrical conduction with increasing silica content.60 Parameters pertinent to the filler content, such as free volume and particle surface chemistry could also be relevant.



Figure 9. DC conductivity of (a) PDMS A and (b) PDMS B before and after post-curing.

### Dielectric spectroscopy

#### Ambient temperature measurements

The real (*ε’*), as well as imaginary (*ε’’*) parts of the complex dielectric permittivity of the two PDMS compounds, at ambient temperature are depicted in Figure 10. Before post-curing the ε’ values of both systems are around 2.8 over a wide frequency range, which is consistent with literature.61 However, these values increase abruptly at the low frequency regime: in the case of PDMS A the increase begins at f < 10-1 Hz, while in PDMS B at f < 10-3 Hz, see Figures 10a and b, respectively. The sharp increase in *ε’* is not evident in the dielectric spectra of the post-cured elastomers. Similarly, the *ε’’* spectra (Figures 10c and d), before post-curing, reveal increasing loss values with descending frequency; in the case of PDMS A the formation of a loss peak at ~10‑2 Hz is also evident. The post-curing seems to result in a drastic reduction of dielectric loss values (up to two orders of magnitude) in the mid-to-low frequency regime in both materials, while the loss peak in PDMS A is not visible upon thermal treatment. Furthermore, the observed *ε’’* effects do not seem to constitute charge transport, which can typically be identified by a slope of -1 in the log-log-scaled plot at the low frequency regime;49 the ε’’ slopes in Figures 10c and d are all below -1. Further analysis such as Nyquist plots and derivative dielectric losses (see Supporting information) suggests that even though there might be some slight effects stemming from charge transport, the losses seen in the tested systems are largely dependent on polarization processes and are affected by the post-curing in two distinct ways; these will be discussed below.



Figure 10. Real (a, b) and imaginary (c, d) parts of the complex dielectric permittivity of PDMS A (a, c) and PDMS B (b, d) before and after post-curing.

Consider first PDMS A: the existence of the loss peak is likely to be the main contributing factor and point of discussion here. It has been reported62 that PDMS features a normal (n) mode relaxation as well as interfacial polarization phenomena occurring at temperatures near ambient. The interfacial polarization effects were claimed to be pertinent to stannous oxide particles and other ionic residues stemming from tin-based catalysts. Since both PDMS systems, in the study presented here, are known to utilize platinum-based catalysts instead we infer to rule out this possibility in the present study. On the contrary, Lewicki et al62 describes the n mode relaxation as a “large-scale cooperative motion” of the PDMS network that was found to be sensitive to alterations in the network mobility and varied with the addition of fillers.62 Even though filler addition did not occur during post-curing in our study, it was shown that terminal vinyl groups are evident in the Raman spectra in PDMS A (see Figure 7) before post-curing, which led to the assumption that some long pendant chains are still present. The latter are expected to affect the network mobility (potentially the n mode relaxation). Indeed, long pendant chains have been shown to influence the dynamic behaviour of PDMS A in the low frequency regime.63–65 The pronounced loss peak in PDMS A, before post-curing, is likely to be attributed to such unreacted “dangling” chains. Other moieties, such as pendant or non-reactive plasticizers66 could also be contributing depending on the composition of PDMS A, however the fact that the loss peak is not evident upon post-curing is not supporting this notion. Furthermore, the possibility that the unreacted vinyl groups in PDMS A could be the ones located on the vinylated silica surfaces is not fully supported, since such functionalities are expected to be much shorter than unreacted pendant PDMS chains and therefore not likely to contribute to such a low-frequency loss peak.

Consider now PDMS B: the observed reduction in ε’ and ε’’ values is likely pertinent to cyclic volatiles removal, even though such moieties might not be expected to cause interfacial effects, as their chemical structure is equivalent to PDMS. If one accounts for stereochemistry, the bond angle at oxygen (Si-O-Si) of cyclic structures could be of crucial concern. As mentioned earlier the average bond angle at oxygen in the PDMS backbone is ~143o.67 Furthermore, the Si-O bond features particularly strong polar and ionic characteristics.68–70 However, only oligomers consisting of five or more silicon atoms (D5 and upwards) display bond angles equivalent to PDMS; the saddle-shaped D4 structures feature oxygen angles of 142o, while the planar-shaped D3 display angles as small as 131.6o, and other cyclic components feature even lower angles down to 105o.71 Structural variations of this magnitude are expected to affect the electrical nature, including polarity, of such components and therefore aid in the rise of electrical heterogeneity within the PDMS matrix. Even though it was speculated, in the FTIR section, that cyclic molecules larger than D3, possibly between D6 – D8, are removed during post-curing, the exact nature of cyclic siloxanes found in the tested systems in this study is not known. It could be assumed that some of those molecules might have been small enough to be causing the abovementioned phenomena, before post-curing, and those are likely to be more prevalent in PDMS B featuring increased volatile content (see Figure 4). If that is the case, then the removal of such small molecules (especially D3) was not observable via our FTIR analysis (see discussion on Figures 5 and 6)

Overall, we deduce that the increased low‑frequency *ε’* and *ε’’* values, observed before post-curing, are attributed primarily to unreacted, long, pendant chains in PDMS A and the existence of low molecular weight volatiles in PDMS B.

#### Temperature dependent measurements

To further support the notion that the post-curing treatment alters the chemistry and structure of the two tested PDMS systems, temperature dependent dielectric spectroscopy was used as a means of observing such effects in a wide temperature range. The temperature dependent dielectric spectra of PDMS A and PDMS B, at a fixed frequency of 1 Hz, are illustrated in Figure 11.

In the case of PDMS A, the *ε’* values (Figure 11a, black squares) mostly vary between 2.5 – 3.5 for a wide range of temperatures (-180 ◦C to 50 ◦C). A peak appears between -120 ◦C and ‑110 ◦C, corresponding to the glass transition temperature (*Tg*).72 The *Tg*-related peak is asymmetric, which is attributed to the crystalline phase of PDMS at the temperature range of -90 ◦C to -30 ◦C.73 Between 50 ◦C and 200 ◦C another prominent peak is evident. Such a feature suggests a slow process related to relatively large dipoles. Based on the previous discussion the *ε’* peak is attributed to vinyl-terminated long PDMS chains. The fact that the permittivity values drop above ~120 ◦C (therefore forming a *ε’* peak) could be ascribed to incorporation of the long pendant chains into the crosslinked network, during the measurement. After the post-curing treatment (Figure 11a, red squares), the prominent high-temperature peak has disappeared. While the location of the *Tg*-related peak in PDMS A is seemingly unaffected, the magnitude of it appears increased, suggesting that further crosslinking might have taken place during the post-curing treatment. The latter phenomenon further suggests that the high-temperature peak, before post-curing, is largely influenced by the long pendant chains. Figure 11c shows the temperature dependent *ε’’* spectra of PDMS A. The observed behaviour before post-curing (Figure 11c, black squares) aligns well with that of *ε’*, as a sharp *Tg*-related peak appears at about -120 ◦C, while a prominent broad peak, appears at higher temperatures, between 20 ◦C and 200 ◦C. The post-curing treatment (Figure 11c, red squares) has a significant effect on the high-temperature peak since it appears to have either shifted out of the observation window or a certain portion of it has been eliminated. As discussed above, the low frequency relaxation (here appearing at the high temperature regime) is likely associated with the unreacted long pendant chains. We are inclined to categorise this relaxation as a distinct mechanism from the abovementioned n-mode relaxation that typically refers to a fully crosslinked network. It is reasonable to assume that incorporation of those unreacted long chains into the crosslinked network would reduce their mobility and shift the associated phenomena to higher temperatures (or lower frequency), as seen in PDMS A after post-curing. Alternatively, if the observed dielectric process is, at least partially, affected by dispersive transport or electrode processes (that was discussed above), then the removal of volatiles (combined with the crosslinking during post-curing) may have triggered a change in the charge carrier mobility and caused variations in the electrode polarization process, explaining the observed behavior.

The temperature dependent *ε’* spectra of PDMS B, at 1 Hz are shown in Figure 11b. This material features an asymmetric *Tg*-related peak at - 100 ◦C, while the high temperature regime is characterised by a gradual permittivity decrease without any other apparent features. Spectra before and after the post-curing are largely similar. Comparison between PDMS A and PDMS B reveals *Tg* values higher in the latter component, that might be related to either larger silica content and/or higher molecular chain; both notions have been supported by the FTIR spectra shown earlier (see discussion on Figure 1). Figure 11d shows the temperature dependent *ε’’* spectra of PDMS B. Similar trends to those described for PDMS A can be seen, albeit with relatively lower dielectric loss values, presumably due to the absence of long pendant chains in the first place. It is reasonable to assume that, here, any observed effects are primarily associated with removal of volatile species. The missing section of *ε’’* spectra in Figure 11d is due the inability of the device to record such low loss values.



Figure 11. Real (a, b) and imaginary (c, d) parts of the complex dielectric permittivity of PDMS A (a, c) and PDMS B (b, d) plotted against temperature, at 1 Hz, before and after post-curing.

The presented temperature dependent spectra support the notion that PDMS A features unreacted pendant long chains before the post-curing and this is shown to be amplifying the magnitude of the observed effects, before and after the thermal treatment. In contrast, PDMS B, that is primarily characterised only by volatiles removal, features relatively milder variations in its dielectric spectra. These findings are in good accordance with the FTIR, Raman and TGA results presented above.

### DC breakdown strength

Figure 12 shows the Weibull probability plots of the DC breakdown strength of the tested materials. It is evident that the post-cured systems display higher breakdown strength than their untreated counterparts. PDMS A shows a notable 13.2% increase of the scale factor (breakdown probability of 63.2%) from 184.8 ± 8.9 kV/mm to 209.3 ± 11.8 kV/mm, as a result of post-curing. PDMS B displays a less significant shift of scale factors upon post-curing, from 191.2 ± 6.9 kV/mm to 210.3 ±16.8 kV/mm (9.9% increase). As discussed in the introduction section, studies in the related literature34,38 have described similar breakdown strength improvements with post-curing treatment. Nevertheless, those studies tend to ascribe this effect solely to volatiles evaporation. However, in the present study it is shown that the increase is more prominent in PDMS A as compared with PDMS B, which is not in line with the volatiles removal shown in the isothermal TGA test (Figure 4). This behaviour is not consistent with the recorded DC conductivity performance either, as shown in Figure 9. Therefore, it is suggested that retained cyclic volatiles are not the primary underlying mechanism and that the structural alterations, such as the ones shown in FTIR (Figures 5 and 6) and Raman (Figures 7 and 8) spectroscopy might be the dominant factor here. Indeed, PDMS A demonstrated larger structural alterations, such as incomplete crosslinking before post-curing, which also had a great effect on the observed dielectric losses (Figures 10 and 11). In fact, it has been claimed23 that the electrical breakdown strength is proportionally related to the elastic modulus in PDMS systems. It is also widely accepted that structural alterations such as integration of long pendant chains (in PDMS A) and elimination of excess crosslinker hydrides (both in PDMS A and B), as discussed earlier, results in increased crosslinking density and therefore stiffness.63 Even though previous related studies34 speculated that no further crosslinking is taking place during post-curing, it is shown here (via FTIR and Raman spectroscopy) that this is quite likely the case and it might be the dominant factor in increasing DC breakdown values. Beyond that, the initiated thermal decomposition, occurring in PDMS A with post-curing, does not seem to be crucial here either, since it features equivalent scale factor with post-cured PDMS B, which did not show signs of decomposition (see discussion on Figures 5 and 6). In contrast, PDMS B exhibits somewhat higher data-point scatter (lower shape factors, slopes in Weibull plots) than PDMS A. More specifically, PDMS A displays shape factors of 16.54 and 14.19 (14.2% decrease), while PDMS B displays shape factors of 11.28 and 10.4 (7.8% decrease), before and after post-curing, respectively. Evidently those variations are not in line with the observed cyclic volatiles removal, as less scatter would be expected with the removal of any kind of impurities. Therefore, we infer that removal of volatiles is not the main contributing factor here either. It is more likely that the compositional differences revealed between the two systems, as shown in FTIR (Figure 1) and Raman (Figure 2) spectroscopy are the main contributing factors, instead. Even though filled only with methylated (therefore more compatible than that in PDMS A) silica, PDMS B is more likely to feature agglomeration effects due to its higher silica content than PDMS A. The latter fact could induce some lower breakdown events (see the low probability tail), consecutively increasing the observed data scatter, even deviating out of the 95% confidence bands in some cases.



Figure 12: Weibull probability plot of the DC breakdown strength of (a) PDMS A and (b) PDMS B, before and after post-curing.

Overall, it appears that the post-curing has a positive effect on the DC breakdown values of both systems. Nevertheless, the removal of cyclic volatiles appears to be less relevant, as previously implied, and that structural or compositional variations induced by the thermal treatment are more relevant.

In summary, the post-curing thermal treatment has been proven beneficial in improving the electrical performance of the two tested PDMS systems and these improvements are pertinent to both: (i) removal of volatile oligomers and (ii) structural variations, such as complete formation of the crosslinked network. Associated schematic illustration is shown in Figure 13.



Figure 13: Proposed structural and chemical characteristics after the: (a) quick curing and (b) post-curing.

# CONCLUSIONS

Two commercial silicone rubbers, named PDMS A and PDMS B (RTV and LSR, respectively) were prepared and tested before and after a post-curing treatment at 200 ◦C for 4h. TGA analysis revealed volatilized mass of ~1.7% and 3.5% in PDMS A and PDMS B, respectively. FTIR and Raman spectroscopy demonstrated structural differences that align well with the supposed composition of the two tested components, while both methodologies additionally revealed beneficial structural and chemical alterations promoted by the post-curing. Before the thermal treatment, both components featured excess crosslinker hydrides, while PDMS A also displayed larger scale structural variations with evidence of unreacted long pendant, vinyl-terminated chains. It was found that the electrical performance of the tested elastomers is primary influenced to either the removal of cyclic volatiles, or the incomplete formation of the crosslinked network. For instance, the DC conductivity values of both silicone elastomers dropped with thermal treatment, and the magnitude of this effect is primarily aligning with the cyclic volatile removal trend. Even though post-curing resulted in reduced low-frequency *ε’* and *ε’’* values in both components, the structural alterations in PDMS A led to more notable effects such as the elimination of a relaxation peak associated with the mobility of unreacted long chains. Lastly, the thermal treatment enhanced the DC breakdown scale factors and reduced the corresponding shape factors, an effect that was found to be strongly affected by variations in structural characteristics (more prominent in PDMS A). The findings of this study demonstrate that outgassing might not be the only underlying mechanism during post-curing of commercial PDMS compounds, since a simple (and often quick) curing suggested by manufacturers does not guarantee formation of a fully crosslinked network and could result in deteriorated performance. The importance of post-curing is outlined whatever the re-enforcing mechanism is.

# Conflict of Interest

The authors declare no conflicts of interest.

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# Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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